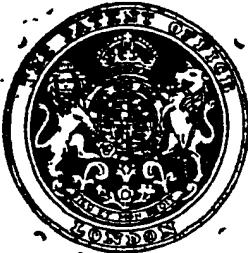


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PATENT SPECIFICATION

676,770



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No. 32600/48.

Application made in United States of America on June 5, 1948.

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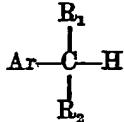
Index at acceptance:—Class 2(iii), C3a13b(1: 2: 5: 6), C3a14a1(a: b), C3a(14a7c: 15).

COMPLETE SPECIFICATION

Improvements in or relating to Phenol Production

We, THE DISTILLERS COMPANY LIMITED, a British Company, of 12, Torpichen Street, Edinburgh, 3, Scotland, Assignees of EERO OLAVI ERKKO and 5 RICHARD STANLEY GEORGE, both Citizens of the United States of America, of 3200, West Second Street, City of Wilmington, State of Delaware, and Centerville Road, H.D. No. 1, City of Wilmington, State 10 of Delaware, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the 15 following statement:—

This invention relates to a process for the conversion of alkyl-substituted aromatic organic compounds having the structural formula:—



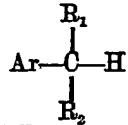
20 to phenols. In the structural formula R₁ and R₂ represent alkyl groups and Ar represents an aryl or alkaryl group. More particularly, the invention relates to a 25 continuous process for the conversion of compounds such as cumene to phenols.

There have been numerous processes developed for the purpose of producing phenols synthetically due to the fact that 30 the demand for phenols, such as the cresols and phenol itself far exceeds the amount which may be recovered in the refining of coal tar. Only a limited number of the processes for the preparation of 35 phenol have proved sufficiently satisfactory to be applicable to commercial production. One of these involves the sulphonation of benzene and the formation of sodium benzene sulphonate which is fused with sodium phenolate. The phenolate upon acidification yields phenol, which may be purified by distillation. However, probably 40 the most widely used commercial process 45 today for the preparation of phenol is that

of hydrolyzing chlorobenzene with aqueous sodium hydroxide under conditions of high temperature and pressure to produce sodium phenolate, which then is acidified to give phenol. The chlorobenzene may be prepared either by direct chlorination of benzene or by chlorination with a mixture of hydrogen chloride and oxygen. 50

Even those processes which have been 55 adapted to commercial production of phenol are not entirely satisfactory. They require large equipment investment and installation to provide facilities for the raw materials used, and they must be 60 operated on the basis of large production capacity in order to produce phenol at a reasonable price. In addition, the processes are disadvantageous because of the many steps involved, the deterioration of 65 equipment due to the use of corrosive raw materials, and the considerable problem of disposal of waste waters contaminated with phenol.

In our copending Application Number 70 32604/48 (Serial No. 676,772) we have described and claimed a process for producing certain tertiary organic hydroperoxides by intimately contacting alkyl-substituted aromatic organic compounds 75 having the structural formula:—



in which R₁ and R₂ represent alkyl groups and Ar represents an aryl or alkaryl group 80 in liquid phase with an oxygen containing gas in the presence of a peroxidic oxidation initiator in the manner set forth in the first step of the present process.

In our copending Application Number 85 32601/48 (Serial No. 676,771) we have described a process of preparing phenols by contacting the above-described tertiary organic hydroperoxides with a catalyst capable of decomposing the hydroperoxides in non-aqueous medium in the 90

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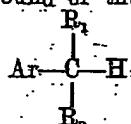
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manner set forth in the second step of the present process.

In the process of the present invention the unreacted alkyl-substituted aromatic organic compound is separated from the other components of the reaction mixture, purified and recycled back to the oxidation step. Thus, there is provided a continuous process of producing a phenol 10 from an alkyl-substituted aromatic organic compound.

Now in accordance with this invention, it has been found that phenols and aliphatic ketones may be prepared simply, efficiently, economically and simultaneously from an alkyl substituted aromatic compound of the formula:



in which R_1 and R_2 represent alkyl groups 20 and Ar represents an aryl or alkaryl group by adding a peroxidic free-radical liberating initiator to said organic compound, contacting the mixture in the liquid phase under anhydrous conditions with a molecular oxygen containing gas to obtain an 25 organic hydroperoxide, contacting the hydroperoxide containing reaction mixture under substantially anhydrous conditions with decomposition agent as 30 hereinbefore defined, separating in known manner the aliphatic ketone, phenol and unreacted alkyl-substituted aromatic compound, purifying said unreacted aromatic compound and recycling the purified compound to the oxidation stage. By 35 "known manner" is understood any method which has been described in the literature or would be known to the skilled chemist to be suitable for the separation 40 of phenol and aliphatic ketone from such hydrocarbons.

The present process is straightforward and is free from all the disadvantages connected with the other processes discussed. 45 In addition to producing phenols, the process at the same time produces aliphatic ketones as valuable products. This also is in contrast to previous processes for preparing phenols.

50 In carrying out the process of this invention, a peroxidic oxidation initiator such as α,α -dimethylbenzyl hydroperoxide is added to cumene, for example, contained in an oxidation unit, and the 55 reaction mixture is agitated vigorously while a stream of air or oxygen is simultaneously passed through the reaction mixture. The oxidation is carried out at a temperature, for example, between 60 about 50° and about 100° C. until standard analytical data indicate that suffi-

cient conversion of the cumene to α,α -dimethylbenzyl hydroperoxide has taken place. The oxidation reaction mixture, which contains the α,α -dimethylbenzyl 65 hydroperoxide and some unreacted cumene, then may be transferred, with or without first stripping the mixture of some of the cumene, to a reactor which is charged with a decomposition catalyst 70 such as an acid-treated bentonite. The oxidation reaction mixture is brought into contact with the catalyst at a temperature of about 20° C., for example, and by so doing the α,α -dimethylbenzyl hydroper- 75 oxide is decomposed to phenol and acetone. Through use of suitable condensation and distillation units the phenol, acetone and unreacted cumene are separated from each other, and the recovered cumene is re- 80 cycled to the oxidation unit for further oxidation after first being purified of any traces of phenol, since the presence of even minute amounts of phenol in the cumene will retard the oxidation of the latter. This purification of the recycle cumene is accomplished either by a very efficient separation during the original distillation in which the cumene and phenol are separated from each other, or 90 by a subsequent distillation of the original cumene distillate.

The following examples constitute specific illustrations of the embodiments of the invention generally outlined above. 95 All amounts are based on parts by weight.

EXAMPLE 1.

The equipment used in this process was composed mainly of 2 units, one for the oxidation and the other for the decomposition reaction. Both units were constructed of stainless steel and each reactor was fitted with suitable condensation and agitation units. In addition, the decomposition reactor was equipped with a distillation unit for separation of the components of the decomposition reaction. The oxidation reactor was charged with 100 502 parts of cumene and there then was added to the cumene 38 parts of oxidized 105 cumene from a previous run, this oxidized cumene containing 46.3% of α,α -dimethylbenzyl hydroperoxide. The reaction mixture was brought to a temperature of 90° C. then oxygen was introduced into the 110 reactor at the rate of about 200 cc./min./kg. of cumene. Samples were taken at periodical intervals for refractive index and hydroperoxide determinations, the 115 hydroperoxide content of the oxidized oil 120 being determined by adding a sample of the oil to acidified potassium iodide and noting the amount of iodine liberated. At the end of 46.5 hours the oxidized oils had a refractive index which indicated a con- 125

version of approximately 51.1% of cumene to oxidized materials and the hydroperoxide content was 50.7%. This oxidation reaction mixture then was transferred to 5 the decomposition reactor which contained 11.2 parts of montmorillonite. The temperature of the reactor and its contents was brought to 100° C. At the end of 3.5 hours the hydroperoxide had decomposed 10 to the extent of 69% and at the end of 7 hours 82%. Upon completion of the reaction the reaction mixture was passed through a filter bed to remove the montmorillonite catalyst and the reaction mixture 15 then was stripped of acetone and the remaining product distilled at a pressure of about 150 mm. of mercury using a reflux ratio of about 5:1. By this distillation the phenol and unreacted cumene 20 were efficiently separated. The recovered cumene was free of phenol and was recycled to the oxidation reactor for further oxidation in combination with additional fresh cumene. The amount of phenol 25 recovered by the distillation was 93% of the theoretical amount based on the amount of hydroperoxide originally present.

EXAMPLE 2.

30 Using the apparatus described in Example 1, 600 parts of cumene (refractive index at 20° C. 1.4905) to which was added 30 parts of oxidized cumene from a previous run, this oxidized cumene containing 35 60% of α,α -dimethylbenzyl hydroperoxide, was oxidized at 50° C. using air at the rate of about 335 cc./min./kg. of cumene. When the oxidized oils had a refractive index of 1.4990, this indicating 40 a conversion of approximately 27.3% of the cumene to oxidized materials, the reaction mixture was transferred to the reactor in which the decomposition was carried out. The oxidized oils contained 25.9% of 45 α,α -dimethylbenzyl hydroperoxide. In the decomposition reactor there then was added to the oxidized oils a solution of 18.1 parts of anhydrous ferric chloride dissolved in approximately 837 parts of 50 anhydrous cumene. Immediate reaction occurred and at the end of 15 minutes the hydroperoxide was completely decomposed as indicated by withdrawing a sample of the reaction mixture and testing for 55 hydroperoxide content by washing the sample with aqueous sodium hydroxide to precipitate the iron, filtering, adding the filtrate to acidified potassium iodide, and noting the amount of iodine liberated. 60 The reaction mixture was worked up as in Example 1 and the yield of phenol was 98% of the theoretical based on the amount of hydroperoxide originally present. As in Example 1, the recovered cumene was 65 recycled to the oxidation unit.

EXAMPLE 3.

The same type of apparatus as used in Example 1 was utilized in the present example with the exception that the oxidation reactor was constructed of nickel. To the oxidation reactor was charged 5000 parts of cumene to which 207 parts of oxidized cumene containing 72.4% of α,α -dimethylbenzyl hydroperoxide had been added. Oxygen was passed through the reaction mixture for 12 hours at a rate of 0.0276 cu. ft./min./kg. of cumene. During the oxidation the temperature within the reactor was maintained at 120° C. and the pressure at 60 lb./sq. in. At the end of 12 hours there was obtained 5984 parts of a crude reaction product which contained 33.4% α,α -dimethylbenzyl hydroperoxide. This reaction product then was transferred to the decomposition reactor which contained 38 parts of an acid-treated bentonite suspended in 500 parts of anhydrous benzene. The oxidation reaction product was gradually added to the suspension of the catalyst. During the resulting decomposition reaction the reaction mixture was maintained at a temperature of 270° C. and the pressure within the reaction vessel at 190 mm. The reaction was complete with 100% decomposition of the hydroperoxide in 20 minutes. The decomposition reaction mixture then was passed through a filter bed to remove the bentonite catalyst and the filtrate distilled at a pressure of 15 mm. The yield of phenol recovered by the distillation was 94.8% of the theoretical based on the amount of α,α -dimethylbenzyl hydroperoxide originally present. There also was obtained, based on the hydroperoxide, a yield of acetone which was 95% of the theoretical, this product being recovered from the condensation units with which the decomposition reactor was equipped. As a result of the distillation the un-reacted cumene was obtained free of phenol and was recycled to the oxidation unit.

EXAMPLE 4.

Using the apparatus described in Example 1, the oxidation unit was charged with 502 parts of cumene (refractive index at 20° C. 1.4912), 38 parts of oxidized cumene containing 46.3% α,α -dimethylbenzyl hydroperoxide and 7.6 parts of sodium *n*-butoxide. Oxygen was passed into the solution at a rate of about 200 cc./min./kg. of cumene. The reaction was carried out at a temperature of 90° C. When the refractive index of the reaction mixture reached a value of 1.5076 the reaction product was transferred to the decomposition reactor. The amount of α,α -dimethylbenzyl hydroperoxide was 51.8% and the total conversion was 57%. 130

To the oxidation reaction mixture there was then added at 20° C. a solution of 27 parts of boron trifluoride-etherate dissolved in approximately 900 parts of anhydrous cumene. Immediate reaction occurred and the temperature of the reaction rose. At the end of 15 minutes a sample of the reaction mixture was withdrawn and tested for hydroperoxide content. No hydroperoxide remained in the reaction mixture. Upon working up the reaction mixture as described in Example 1, phenol was obtained in an amount which was 95% of the theoretical yield based on the amount of hydroperoxide originally present.

EXAMPLE 5.

Using an apparatus similar to that of Example 1, the apparatus was charged with 575 parts of cumene (refractive index at 20° C. = 1.4926). To the cumene was added 25 parts of oxidized cumene containing 80% of *a,a*-dimethylbenzyl hydroperoxide. There also was added 1 part of sodium hydroxide pellets. The reaction mixture was brought to a temperature of 90° C. and oxygen was passed through the mixture at a rate of about 175 cc./min./kg. of cumene. At the end of 24 hours the reaction mixture had a refractive index of 1.5023, this indicating a conversion of approximately 38.7% and the hydroperoxide content was 34.4%. The oxidation was continued for a total of 41 hours elapsed time, at the end of which the reaction product had a refractive index of 1.5091, this indicating a conversion of about 61.8%. The hydroperoxide content was 53%. The oxidation reaction mixture then was transferred to the decomposition unit which was charged with 200 parts of an acid-treated bentonite. The oxidation reaction mixture was slowly dropped on the bentonite which was heated to a temperature of 360° C. The pressure in the system was maintained at 36-44 mm. Distillation of the material collected in the condensation units resulted in a yield of phenol which was 69.8% of the theoretical.

EXAMPLE 6.

The apparatus of example 1 was utilized and to the oxidation unit were added 400 parts of diisopropylbenzene and 2 parts of benzoyl peroxide. The reaction mixture was heated to 90° C. and oxygen was passed through the mixture at a rate of 250 cc./min./kg. of diisopropylbenzene. When the refractive index reached a value of 1.4939 the reaction product was transferred to the decomposition unit. The reaction product contained 17% of *a,a,a',a'*-tetramethyl-*p*-xylylene dihydroperoxide. To the oxidation reaction mixture there was added 4.2 parts

of an acid-treated bentonite. The reaction mixture was stirred at 20° C. for 1.5 hours, then heated slowly to 76° C. over a period of 7 hours. During this period there were added to the reaction mixture 3 additional portions, 3 parts each, of the acid-treated bentonite catalyst. At the end of this time the dihydroperoxide had decomposed to the extent of 84.8%. The reaction mixture was passed through a filter bed to remove the catalyst, then the filtrate was stripped of the benzene, acetone, and a portion of the unreacted diisopropylbenzene. The remaining material was distilled at a pressure of 1.0 mm., there being obtained hydroquinone in a yield which was 65% of the theoretical based on the amount of dihydroperoxide. The combined portions of recovered diisopropylbenzene were redistilled, then the purified material was recycled to the oxidation unit.

EXAMPLE 7.

Utilizing the apparatus described in Example 1 and following the procedure of Example 6, 400 parts of *p*-cymene to which had been added 4 parts of *t*-butyl hydroperoxide was oxidized until the reaction product had a refractive index of 1.4960. This reaction product contained 10% *a,a*-dimethyl-*p*-methylbenzyl hydroperoxide. After being transferred to the decomposition unit, the oxidation reaction product was brought into contact with a suspension of 1.7 parts of an acid-treated bentonite in 40 parts of anhydrous benzene. The initial temperature and pressure were 24° C. and 760 mm. The rate of reaction was increased by lowering the pressure to 100 mm. and raising the temperature to 38° C. Upon completion of the decomposition reaction, the reaction mixture was distilled at a pressure of 12 mm. The yield of *p*-cresol recovered by the distillation was 81% based on the amount of *a,a*-dimethyl-*p*-methylbenzyl hydroperoxide originally present. The *p*-cymene recovered by the distillation was given a wash with a small amount of 10% aqueous sodium hydroxide in order to remove traces of *p*-cresol. After being dried the purified *p*-cymene was recycled to the oxidation unit.

EXAMPLE 8.

Using the apparatus of Example 1, 120 cumene was continuously fed into the oxidation unit, the amount of cumene in the unit being maintained at the level of about 5000 parts by weight. Within the unit the oxidation was carried out continuously, using oxygen as the oxidizing agent, at a temperature of 120° C. and a pressure of 60 lb./sq. in. The flow of oxygen through the reaction mixture was maintained at 0.0276 cu. ft./min./kg. of 130

cumene. The oxidation reaction originally was initiated by addition of 200 parts of oxidized cumene containing 75% of α,α -dimethylbenzyl hydroperoxide to the original charge of 5000 parts of cumene. No further addition of initiator was necessary as long as the oxidation was maintained in operation. After the oxidation reaction once had been started and the amount of α,α -dimethylbenzyl hydroperoxide had reached the level of about 30% by weight based on the total charge, the hydroperoxide content was maintained at this level and a portion of the reaction product continuously withdrawn into the decomposition unit. Within the decomposition unit the pressure was maintained at 200 mm. Simultaneously with the introduction of the oxidation reaction product, there was fed into the decomposition unit a slurry of an acid-treated bentonite in cumene, the amount of the bentonite catalyst being about 2% based on the amount of hydroperoxide being introduced. The decomposition was carried out continuously by this procedure, the heat of reaction being sufficient to maintain the temperature at the desired level. The catalyst was constantly removed from the cumene slurry by means of centrifuging, the acetone was recovered from the condensation units, and the phenol-unreacted cumene reaction mixture was continuously fed into a distillation unit which was operated at a pressure 150 mm. and a reflux ratio of 5. The cumene recovered from the distillation was fed back to the oxidation unit as part of the cumene utilized to maintain the oxidation unit in constant operation. The phenol obtained from the distillation of the phenol-unreacted cumene mixture was subjected to additional distillation under a pressure of 100 mm. and using a reflux ratio of 3. The overall yield of phenol was 95% of the theoretical based on the amount of cumene. On the same basis the yield of acetone was 93.5%.

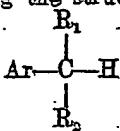
Although the examples have set forth the use of cumene, *p*-cymene and diisopropylbenzene as the materials to which the oxidation has been applied, other compounds having the structural formula previously set forth for the alkyl-substituted aromatic organic compounds may be utilized. Exemplary of such are *sec*-butylbenzene, *p*-ethylisopropylbenzene, and isopropynaphthalene. The main requirement for the compounds which may be oxidized in accordance with this invention is the presence of a tertiary carbon atom carrying a hydrogen atom as its fourth substituent. As shown by the structural formula, the carbon atom is tertiary because it is directly connected to

three other carbon atoms contained in the groups represented by R₁, R₂ and Ar. The aryl and alkaryl groups need not be derived from benzene as is the case in *p*-cymene, cumene, diisopropylbenzen, and *sec*-butylbenzene. Compounds containing aromatic nuclei such as those derived from naphthalene, anthracene and phenanthrene also are operable, but these compounds, being solids, must be dissolved in a suitable solvent, such as benzene, during the liquid phase oxidation. In addition, the aryl group may be substituted with alkyl groups, as illustrated by the methyl group in *p*-cymene and the iso-propyl group in diisopropylbenzene, and the groups may, for example, be methyl, ethyl, propyl, isopropyl, butyl, isobutyl, secondary butyl or tertiary butyl. The alkyl groups, as represented by R₁ and R₂ in the structural formula, also need not be limited to the methyl groups of *p*-cymene, cumene, and diisopropylbenzene. Other alkyl groups, such as those previously indicated as suitable for substitution in the aryl groups, may be utilized, and R₁ and R₂ may be either the same or different.

The examples have set forth the use of molecular oxygen and air as the oxygen-containing gas, but the oxygen may be furnished also in mixtures of oxygen with nitrogen or other inert gases. Oxygen, when used alone, may be in the form of pure or commercial oxygen. Air may be utilized as it is readily available, but it, as well as the molecular oxygen or oxygen-inert gas mixtures, should be dry. Furthermore, it is advisable, but not necessary, to wash the air with a caustic solution in order to remove carbon dioxide. The rate of input of the oxygen-containing gas may vary within a wide range, depending on the concentration of oxygen in the gas, the pressure at which the oxidation is carried out, and the efficiency of dispersion. In general, at atmospheric pressure the rate of input will vary from about one liter to about 100 liters per hour per kilogram of the alkyl-substituted aromatic organic compound, a preferable range on this basis being from about 5 to about 25 liters per hour per kilogram. At super-atmospheric pressures, for example, 50 to 200 pounds per square inch, the rate of input may be from about 50 to about 350 liters per hour per kilogram of the alkyl-substituted aromatic organic compound, a preferable range being from about 50 to about 280 liters per hour per kilogram.

One of the essential features of the process of this invention is the step of carrying out the oxidation in the presence of a peroxidic free-radical oxidation initiator such as a tertiary organic hydro-

peroxide having the structural formula



as previously described. As indicated by the structural formula of these hydroperoxides, the same limitations as to substituent groups apply as in the case of the structural formula representing the alkyl-substituted aromatic organic compounds which may be oxidized. In other words, 10 these hydroperoxides which may be used as initiators in the process of this invention are the hydroperoxy derivatives obtained by the oxidation of the alkyl-substituted aromatic organic compounds 15 previously described. Exemplary of these hydroperoxides which may be utilized in initiating the oxidation process of this invention are α,α -dimethylbenzyl hydroperoxide, obtained by the oxidation of 20 cumene, α,α -dimethyl- p -methylbenzyl hydroperoxide, obtained by the oxidation of p -cymene, α,α -dimethyl- p -isopropylbenzyl hydroperoxide and $\alpha,\alpha,\alpha^1,\alpha^2$ -tetra-methyl- p -xylylene dihydroperoxide, both 25 obtained by the oxidation of p -diisopropylbenzene, and α,α -dimethylnaphthalenylmethyl hydroperoxide obtained by the oxidation of isopropylnaphthalene. These hydroperoxide initiators, which 30 may be named as α,α -dialkylaryl methyl hydroperoxides, may be added to the compound being oxidized in the form of the pure hydroperoxide but, as shown by the examples, it is advantageous also to add 35 the hydroperoxides in the form of those hydroperoxide-rich oils obtained from a previous oxidation. The concentration of the hydroperoxide in the hydroperoxide-rich oils may be increased, however, by 40 removing some of the hydrocarbon initially oxidized by fractional or steam distillation.

In addition, however, to the above-described initiators, which preferably are 45 utilized because they are the type of hydroperoxide obtained in the oxidation process of this invention, there may be used any peroxidic substance which is capable of initiating a free radical oxidation 50 chain under the conditions utilized. In general, there therefore may be used any organic peroxide, hydroperoxide or other peroxidic compound capable of decomposing to form organic free radicals. 55 Illustrative of such peroxidic materials are acetyl peroxide, benzoyl peroxide, tri-phenylmethyl peroxide, t -butyl peroxide, t -butyl hydroperoxide, t -amyl hydroperoxide, diphenylmethyl hydroperoxide, 60 tetralin hydroperoxide, triphenylmethyl hydroperoxide, α,α -dimethylcyclopentyl

hydroperoxide, methylcyclohexyl hydroperoxide, cyclohexene hydroperoxide, and naphthene hydroperoxides. These peroxidic materials therefore include the acyl, 65 aroyl, dialkyl, and diaralkyl peroxides; and the alkyl, aralkyl, cycloalkyl and cycloalkenyl hydroperoxides. Other free radical initiators, such as hexaphenyl-ethane, which are converted into peroxidic materials during the oxidation process of this invention, also are operable. 70

The concentration of the peroxidic initiator may be varied over a fairly broad range. Using the hydroperoxides prepared during the process of this invention as an example, if the hydroperoxide is furnished in the form of a hydroperoxide-rich oil, the amount of oil may vary from about 1 to about 50%, based on the alkyl-substituted aromatic organic compound, but a preferable range on this basis is from about 2 to about 20%. The amount of hydroperoxide-rich oil necessary will depend, of course, upon the concentration 80 of the hydroperoxide in the oil. A smaller amount of an oil containing a high concentration of hydroperoxide will be necessary than will be the case wherein an oil containing a low concentration of hydroperoxide is used. If a pure or substantially pure hydroperoxide is used in initiating the oxidation reaction, the concentration, based on the amount of alkyl-substituted aromatic organic compound, may be 85 varied from about 0.01 to about 20%, a preferable range being from about 0.1 to about 10%. A particularly applicable amount of pure hydroperoxide is about 90 3%. When initiating the oxidation of an alkyl-substituted aromatic organic compound according to the process of this invention, it is preferable to use as the initiator the hydroperoxide obtained by oxidation of the same aromatic organic compound. For example, in the oxidation of cumene, it is preferable to initiate the reaction by the addition of α,α -dimethylbenzyl hydroperoxide. However, when any of the other peroxidic initiators which are 10: 11 operable in the process of this invention are utilized, their concentration relative to the compound being oxidized may be the same as that set forth for the preferred hydroperoxides.

As shown in Examples 4 and 5, the oxidation may be carried out in the presence of an alkaline stabilizing agent. In general, any alkaline material may be used which does not reduce or react with the hydroperoxide product. The examples have shown the use of sodium n -butoxide and sodium hydroxide, but there also may be used other alkali metal and alkaline earth metal hydroxides, alkoxides, and also salts of these metals with weak inorganic 12

and organic acids. As examples of the alkali metal and alkaline earth metal hydroxides, there may be mentioned sodium hydroxide, potassium hydroxide, lithium hydroxide, calcium hydroxide, barium hydroxide, strontium hydroxide, and magnesium hydroxide. The alkoxides are represented by sodium methoxide, sodium ethoxide, sodium isopropoxide, sodium-n-butoxide, and the corresponding potassium, lithium, calcium, strontium, barium and magnesium alcoholates. Exemplary of the alkali metal salts of weak inorganic acids are sodium tetraborate, trisodium phosphate, and potassium carbonate. Examples of alkali metal salts of weak organic acids are those alkali metal salts of acids which form soaps, such as the higher fatty acids, for example, stearic, oleic, palmitic, lauric, linoleic, ricinoleic, the commercially available mixtures obtained by the hydrolysis or saponification of commercial oils and fats; the resin acids or commercial rosins and their modifications, such as dihydroabietic acid, tetrahydroabietic acid, dehydroabietic acid, hydroxytetrahydroabietic acid, hydrogenated rosin, disproportionated or dehydrogenated rosin, and polymerized rosin; and the naphthenic acids.

The amount of the alkali stabilizing agent which may be used may, in general, be from about 0.1 to about 5%, based on the alkyl-substituted aromatic organic compound. A preferable range on this basis is from about 1 to about 3%.

The temperatures at which the oxidations are carried out are quite critical in obtaining optimum yields of hydroperoxides. The temperatures which actually may be used, however, will depend on the pressure existing during the oxidations. Upon the basis of atmospheric pressure, the temperature should be in the range of about 50° to about 100° C., a more desirable range being between about 65° and about 90° C., and a particularly advantageous range being between about 75° and about 90° C. The minimum temperature at 50° C. is necessary since the rate of reaction at, for example, room temperature, is too slow to be of commercial significance in the process of this invention. On the other hand, if the temperature during oxidation is too high, the reaction occurs in such a manner as to result in the formation of considerable by-products. There may be, for example, an excessive amount of ketone formed. In the case of cumene, for example, oxidation at high temperatures at atmospheric pressure will result in the formation of considerable amounts of acetophenone, consequently, the maximum

temperature which should be used at atmospheric pressure in order to obtain high yields of hydroperoxides and minimum ketone formation is 100° C.

Temperatures greater than 100° C. may be used, however, in the oxidation, provided the pressure is increased to greater than atmospheric. Although elevation of the temperature during the oxidation to greater than 100° C. will cause increased decomposition of the hydroperoxides to ketones, this is offset by the increased rate of hydroperoxide formation caused by the elevation of the pressure. In other words, by proper selection of pressure, temperatures above 100° C. may be used during the oxidation to obtain in shorter lengths of time oxidation reaction products having hydroperoxide and ketone contents as desirable as those reaction products obtained at a temperature of 100° C. or less. The amount of ketone will not be out of proportion to the amount of hydroperoxide. Using pressure greater than atmospheric, the oxidation therefore may be carried out at temperatures between about 50° C. and about 150° C., a more desirable range being between about 65° C. and about 140° C., and a particularly advantageous range being between about 75° C. and about 130° C.

The pressures which can be utilized during these oxidations carried out at greater than atmospheric pressures are limited only by equipment design. From a practical standpoint, pressures from atmospheric up to about 500 lb./sq. in. are feasible. A preferable range is from about 50 to about 200 lb./sq. in.

Since the reaction is heterogeneous, suitable agitation is necessary. It is particularly important to bring the air, oxygen, or other oxygen-containing gas into intimate contact with the liquid phase, and this may be effected by using high-speed stirrers, suitable nozzles, porous plates or their combinations.

The course of the reaction may be followed by taking samples at intervals and determining the refractive index of the oily material. In the oxidation of cumene, for example, refractive index values between about 1.5020 and about 1.5145 indicate that about 40 to about 80% of the original organic material has been oxidized and the reaction then is advisably interrupted. Conversions from about 40 to about 70% can easily be obtained in the process of this invention and high hydroperoxide yields may be obtained best by carrying the conversion up to at least about 50%.

The oxidation step of this invention affords a means of obtaining high yields

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of α,α -dialkylarylmethyl hydroperoxides while at the same time minimizing the formation of other reaction products such as the corresponding alcohols. The particular type of oxidation described makes it possible to maintain the difference, or "spread", between total conversion to oxygenated products and actual yield of hydroperoxide at a minimum. The maximum spread under the least desirable conditions of the process will not be greater than about 10%, and by proper selection of conditions the spread may be reduced to 1% or less. It is entirely possible by the oxidation procedure of this invention to obtain substantially complete conversion to the hydroperoxide product. This has not been possible by previous oxidation procedures. The latter generally have used catalysts such as ultraviolet light or heavy metal oxidation catalysts to increase the rate of oxidation and the total conversion to oxygenated products, but such catalysts have also increased the amount of decomposition of the hydroperoxides, thereby lowering the yield of the latter. In other words, the spread between total conversion and actual hydroperoxide yield has been great, and the reaction product consequently has been unsatisfactory due to the existence of considerable amounts of secondary reaction products. Some prior processes also have used an aqueous phase during the oxidation to hinder the formation of certain undesirable reaction products such as substituted styrenes, which would polymerize to wasteful and annoying oxidation residues, but such aqueous phases decrease the rate of oxidation and under certain conditions cause decomposition of the hydroperoxides. The oxidation procedure of the present invention, being carried out under anhydrous, non-catalytic conditions, in the presence of a peroxidic oxidation initiator capable of initiating a free radical oxidation chain, and with intimate contact of the compound being oxidized with sufficient amounts of the oxygen containing gas, obviates all of the difficulties of other processes in obtaining high hydroperoxide yields to the practical exclusion of secondary reaction products. It is apparent that the very nature of the oxidation insures its being economical, and in addition there is no problem of separating the reaction product from a solid catalyst or an additional liquid phase.

The oxidation according to this invention apparently proceeds by a peroxide mechanism. Using cumene as an example, when this compound is oxidized

with molecular oxygen, a hydroperoxide is formed on the tertiary carbon atom of the isopropyl group. In the presence of the small amount of peroxidic initiator utilized in accordance with this invention the formation of the hydroperoxide on the tertiary carbon of the isopropyl group is facilitated. A very small fraction of the peroxidic initiator decomposes in the initial stages of the oxidation, resulting in the formation of free radicals which are sufficient to initiate the formation of hydroperoxide molecules from the cumene. Utilization of the peroxidic initiator during the oxidation step of the process of this invention prevents inhibition and the existence of an induction period.

In carrying out the decomposition step of this invention, several different modifications of the α,α -dialkylarylmethyl hydroperoxides prepared in the oxidation step may be utilized. The entire process being continuous, the most convenient form of the hydroperoxide is that existing in the crude reaction mixture obtained from the oxidation step. In carrying out the oxidation step the oxidation usually is interrupted before all of the hydrocarbon has reacted in order to avoid or limit side reactions. In this manner, the α,α -dialkylarylmethyl hydroperoxide is obtained in mixture with smaller or larger amounts of the original hydrocarbon, which is an α,α -dialkylarylmethane. Such reaction mixtures may be used *per se* in the decomposition step of the process of this invention. The amount of unreacted hydrocarbon remaining in the oxidation reaction product then will act as solvent during the decomposition reaction of the hydroperoxide.

In the case it is desirable, however, to obtain the hydroperoxide in a more concentrated form, the hydroperoxide may be separated from the other constituents of the crude oxidation reaction mixture. The hydroperoxides may be separated from the oxidation reaction mixtures by, for example, fractional distillation at very low pressures, of the order of 0.01 to 1.0 mm. of mercury, the hydroperoxides having higher boiling points than the related hydrocarbon, alcohol and ketone. In some instances the hydroperoxides also may be separated from the oxidation reaction mixtures by crystallization, which may be facilitated by first distilling off at least part of the hydrocarbon. Another method of separating the hydroperoxide from the oxidation reaction mixture involves precipitation of the hydroperoxide with a concentrated aqueous solution (25 to 40%) of sodium hydroxide. The precipitate is crystalline. The pre-

cipitate of α,α -dimethylbenzyl hydroperoxide, for example, analyzes for the sodium salt of the hydroperoxide associated with four molecules of water.

5 The process of this invention therefore is applicable not only to pure or concentrated hydroperoxides but also to mixtures containing varying amounts of the hydroperoxides, for example, the 10 crude reaction mixtures obtained in the oxidation of the alkyl-substituted aromatic organic compounds previously described. In addition, either the pure or concentrated hydroperoxides or the 15 crude reaction mixtures containing the hydroperoxides may be dissolved in a suitable organic solvent which is inert to any of the reactants, products or reaction conditions involved in the decomposition 20 step of the process of this invention. In other words, the solvent should be non-reactive, under the conditions of reaction, to the hydroperoxide, the catalyst, and any of the phenolic or ketonic reaction 25 products obtained by the decomposition. Exemplary of such solvents are the aliphatic, cycloaliphatic, and aromatic hydrocarbons such as pentane, hexane, heptane, isoctane, cyclohexane, cyclon- 30 butane, cycloheptane, benzene, toluene, xylene, cumene, and diisopropylbenzene. Other operable solvents include alcohols, ketones, ethers, esters, and liquid chlorinated hydrocarbons. Exemplary of these 35 are chloroform, carbon tetrachloride, ethylidene dichloride, ethylene dichloride, methanol, ethanol, propanol, cyclohexanol, acetone, methyl ethyl ketone, diethyl ketone, cyclohexanone, methyl 40 acetate, ethyl acetate, butyl acetate, diethyl ether, ethyl methyl ether, dipropyl ether and dibutyl ether. In addition, various acidic solvents, such as 45 glacial acetic acid, which are inert in the process but which may exert some catalytic activity may be used. Where such an acidic solvent is employed, the amount of other catalyst may be reduced. The 50 concentration of the solvent and the α,α -dialkylaryl methyl hydroperoxide in the solution to be used during the decomposition reaction may be varied very widely. The concentration of the hydroperoxide is limited, in other words, only by the 55 reactivity of the hydroperoxide during the decomposition, the effectiveness of the catalyst, and the temperature and pressure used. In other words, the concentration of the hydroperoxide may be 60 selected so that under the desired reaction conditions the conversion takes place at a controllable rate to give a satisfactory amount of conversion product.

The decomposition reaction also may be 65 carried out, as shown in Example 5, in

the vapor phase. The hydroperoxide may be vaporized in the presence or absence of a volatile solvent, and brought into intimate contact with the catalyst and the decomposition will readily occur. The 70 vapor process is advantageous in that the phenol product can be vaporized immediately from the reaction zone, but it is important in such a process that the product not be permitted to remain in the 75 reaction zone for a long period of time since this will result in the formation of undesirable by-products.

In all instances, whether the decomposition reaction be carried out in the vapor 80 or liquid phase, the reaction medium should be substantially anhydrous since the presence of water inhibits, and in many instances completely halts the reaction. The amount of water which can 85 be tolerated in any particular instance will depend on the reactivity of the hydroperoxide, the activity and amount of the catalyst, and the temperature and pressure during the reaction. An amount 90 of water up to about 10% based on the weight of the total reaction mixture may be tolerated under optimum conditions involving high temperature, low pressure and the use of a highly reactive catalyst. 95 However, the amount of water in the reaction mixture ordinarily should not be more than about 5%. Less than about 2% is preferable, and for optimum results water should be completely absent. 100 Removal of water from the reaction mixture during the reaction may be facilitated, as shown by some of the examples, by using reduced pressure. The water 105 also may be removed by addition of a drying agent, such as calcium chloride, calcium sulfate and calcium oxide, to the reaction mixture, or by blowing a dry gas, such as air or nitrogen, through the reaction mixture. 110

In the decomposition step of the process of this invention the catalysts which may be used for decomposing the α,α -dialkylaryl methyl hydroperoxide to a phenol in non-aqueous medium are (besides those shown in the above examples and consisting of montmorillonite, anhydrous ferric chloride, acid treated bentonite, boron trifluoride) kaolinite (Peerless clay), vermiculite, silica gel, kaolin, fuller's earth, diatomaceous earth, halloysite, phosphoric acid on alumina, titanium oxide, phosphorus trichloride, phosphorus pentachloride, phosphorus oxychloride and phosphorus pentoxide; furthermore 125 basic oxides such as alumina; Friedel-Crafts catalysts such as aluminium chloride, zinc chloride, stannic chloride and magnesium chloride, all of which may be supported on carriers which them- 130

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5 selves may have catalytic activity; surface active substances such as the silicates, silica gel, kieselguhr, hylosilicates, and bauxite, phosphoric acid on fuller's earth
 10 or silica; inorganic acids, for example, hydrogen chloride and organic acids; for example, picric acid, chlorine substituted acetic acids; namely, trichloroacetic acid, dichloroacetic acid and chloroacetic acid, and also acid treated clay.

The concentration of the catalyst based on the hydroperoxide will depend on the reactivity of the catalyst, the temperature of reaction and the desired reaction time. The concentration may be varied widely, in other words, but generally may be from about 0.01% to about 200%. A preferable catalyst concentration on this basis is from about 1% to about 20% and a particularly applicable amount in most instances is about 5%. In the case of those catalysts wherein it is possible to calculate their molar concentrations relative to the hydroperoxide, the range of catalyst concentration may be expressed as from about 0.01 mole per cent to about 200 mole per cent based on the hydroperoxide, a preferable range on this basis being from about 1% to about 10%. In continuous operation the ratio of catalyst to hydroperoxide at any particular instant may be as high as 100 to 1, depending upon the design of the reactor, the size of the catalyst particles, and the rate of flow of the hydroperoxide over the catalyst bed. As shown by the examples, the catalyst may be utilized in the reaction either *per se* or dissolved or suspended in a suitable solvent. Particularly in the case of those catalysts which are solids and therefore used as suspension in a solvent it is desirable that efficient agitation be utilized in order to bring the hydroperoxide into close contact with the catalyst. Such agitation may be obtained through use of mechanical stirrers or by passing a stream of a gas such as air through the reaction mixture. The activity of the catalyst increases with its acidity. In general, the more acid the catalyst, the more rapid will be the decomposition reaction, but basic catalysts may be quite effective.

The temperature which may be used during the decomposition reaction may be varied widely, depending upon, mainly, the activity of the catalyst. Some of the catalysts which are operable in accordance with the process of this invention are not extremely reactive at relatively low temperatures, for example, 20° C. to 50° C., but are operable at higher temperatures, for example, 100° C. The temperature at which the reaction is carried out therefore will depend upon the

particular catalyst utilized. However, generally speaking, the decomposition reaction may be effected over a temperature range of about -80° C. to about 400° C. A preferable temperature range within which the reaction may be carried out in liquid phase is about 0° C. to about 200° C., and a particularly applicable temperature for a liquid phase system and a relatively efficient catalyst is about 7 20° C. When the decomposition reaction is carried out in the vapor phase a preferable temperature range is about 150° to about 350° C.

Most of the examples have shown the decomposition reaction as being carried out at atmospheric pressure but some of the examples have shown the use of reduced pressure. It has been found that in some instances the rate of reaction is increased by carrying out the decomposition under reduced pressure since this helps to remove any trace of water which may exist in the reactants or which may be formed during the reaction itself. It is obvious, of course, that the reaction also may be carried out under pressures greater than atmospheric. A broad range of pressure conditions is possible in effecting the decomposition reaction, but from the standpoint of practicability, the reaction preferably is carried out either at atmospheric or slightly less than atmospheric pressure.

The continuous process of this invention is advantageous in its simplicity. Using cumene as an example, the cumene is continuously oxidized, a portion of the oxidation reaction mixture, containing *a,a*-dimethylbenzyl hydroperoxide, constantly withdrawn and transferred to the decomposition unit wherein the hydroperoxide is decomposed immediately, and the phenol and acetone reaction products and unreacted cumene are recovered, the unreacted cumene then being fed back to the oxidation unit to make up part of the cumene feed. The cumene recovered from the decomposition reaction mixture is freed of any contaminating phenol before being recycled to the oxidation unit, and this may be accomplished, as shown by the examples, either by efficient fractional distillation or by chemical treatment, such as washing out the phenol with a dilute aqueous caustic alkali solution. The traces of phenol also may be removed from the recycle cumene by precipitation with liquid ammonia.

One outstanding advantage of the present process over other processes for the production of phenol lies in the fact that it is carried out under substantially anhydrous conditions. This is in direct contrast to the aqueous systems which

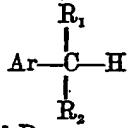
necessarily must be used when phenol is obtained by the hydrolysis of, for example, chlorobenzene or benzene sulfonate. In those processes involving such a hydrolysis, the aqueous phase necessarily is contaminated with phenol and there therefore exists a large problem in plants operating such processes for the disposal of the phenol-contaminated waste water, since the presence of phenol in water generally is undesirable, as when the water later may be utilized for drinking purposes.

The process in accordance with this invention represents a more economical and efficient means for obtaining not only phenol itself but also other phenolic compounds such as *p*-cresol and hydroquinone. The latter two compounds are, of course, obtained by the decomposition of *a,a*-dimethyl-*p*-methylbenzyl hydroperoxide and *a,a,a',a'*-tetramethyl-*p*-xylylene dihydroperoxide, respectively. Due to the simple nature of the process, the latter will be found particularly applicable to small scale installations and will not require the vast outlay of capital and equipment required by previous processes.

Reference is made to British Patent Specification No. 626,095 which was not published before the date of this application wherein the oxidation is carried out in the absence of an added free radical liberating initiator and the decomposition is effected by means of acid.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed we declare that what we claim is:

1. The process of preparing a phenol from an alkyl-substituted aromatic compound of the formula



in which R_1 and R_2 represent alkyl groups and Ar represents an aryl or alkaryl group which comprises adding a peroxidic free-radical liberating initiator to said organic compound, contacting the mixture in the liquid phase under anhydrous conditions with a molecular oxygen containing gas to obtain an organic hydroperoxide, con-

tacting the hydroperoxide containing reaction mixture under substantially anhydrous conditions with a decomposition agent as hereinbefore defined, separating in the known manner as hereinbefore defined the aliphatic ketone, phenol and unreacted alkyl-substituted aromatic compound, purifying said unreacted aromatic compound and recycling the purified compound to the oxidation stage.

2. Process according to claim 1, in which air or oxygen is used as the oxygen-containing gas.

3. Process according to claim 1 or 2, in which the decomposition of the hydroperoxide is carried out under a pressure less than atmospheric.

4. Process according to claim 1, 2 or 3 in which the catalyst is an organic acid catalyst.

5. Process according to claim 1, 2 or 3, in which the catalyst is an acid-treated clay.

6. Process according to any of the preceding claims, which comprises the preparation of phenol from cumene.

7. Process according to claim 6, in which the initiator is *a,a*-dimethylbenzyl hydroperoxide.

8. Process according to any of claims 1—5 which comprises the preparation of *p*-cresol from *p*-cymene.

9. Process according to claim 10, in which the initiator is *a,a*-dimethyl-*p*-methylbenzyl hydroperoxide.

10. Process according to any of claims 1—5, which comprises the preparation of hydroquinone from *p*-diisopropylbenzene.

11. Process according to claim 10, in which the initiator is *a,a*-dimethyl-*p*-isopropylbenzyl hydroperoxide.

12. Process according to any of the preceding claims, in which an aliphatic ketone is added to the reaction mixture.

13. The process of preparing a phenol from an alkyl-substituted aromatic organic compound, substantially as described with reference to the foregoing examples.

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